

Molecular Spectroscopy of Small Free Molecules

- “Small” usually means 2-3 atoms
 - Can mean more if there is a lot of symmetry.
- “Free” means no other atoms or molecules close enough to perturb the intramolecular potential.
- Concepts developed can be extended to larger molecules.

Classification of Spectroscopy by Molecular Motions

- We need to be able to describe how molecules move.
- A molecule of N atoms have $3N$ degrees of freedom
 - Translational (three degrees of freedom)
 - Rotational (three degrees of freedom if nonlinear; two degrees of freedom if linear)
 - Vibrational (all remaining degrees of freedom)

Principal Moments of Inertia

- First need the centre of mass.
 - Define coordinates of the centre of mass as (X, Y, Z) such that:

$$\sum_{i=1}^N m_i(x_i - X) = 0$$

$$\sum_{i=1}^N m_i(y_i - Y) = 0$$

$$\sum_{i=1}^N m_i(z_i - Z) = 0$$

- Then we can treat the translational motion of the molecule as a whole as the motion of a mass $M = \sum_{i=1}^N m_i$ located at (X, Y, Z) .
- This leaves $3N - 3$ coordinates.

Rotational Motion

- Define a coordinate system $(\bar{x}, \bar{y}, \bar{z})$ through the center of mass and choose the orientation of an axis such that:

$$\sum_{i=1}^N m_i \bar{x}_i \bar{y}_i = 0$$

$$\sum_{i=1}^N m_i (\bar{x}_i^2 + \bar{y}_i^2) \neq 0$$

- This is the principal inertial axis system.
 - Usually use (a, b, c) instead of $(\bar{x}, \bar{y}, \bar{z})$
- (a, b, c) is situated in space relative to an external frame of reference with its orientation described by three angles.

- This gives us three principal moments of inertia.

$$I_a = \sum_{i=1}^N m_i (b_i^2 + c_i^2)$$

$$I_b = \sum_{i=1}^N m_i (a_i^2 + c_i^2)$$

$$I_c = \sum_{i=1}^N m_i (a_i^2 + b_i^2)$$

Linear and Nonlinear Molecules

- For a nonlinear molecule, all three of these are nonzero.
 - Therefore $3N - 6$ degrees of freedom still to be accounted for.
- For a linear molecule, only two of these are nonzero.
 - Therefore $3N - 5$ degrees of freedom still to be accounted for.
 - I_a is chosen such that $I_a = 0$. Therefore $b_i = c_i = 0$ and $I_b = I_c$
- The remaining degrees of freedom are internal vibrational degrees of freedom.

The above describes the motion of atoms in terms of classical mechanics.

- Quantum mechanics is used to describe the electronic degrees of freedom and the spin degrees of freedom.
- In spectroscopy we are concerned with the spacing of energy levels.

How are the different types of energy levels spaced?

Spacing of Electronic Energy Levels

- From a quantum mechanical perspective, it is useful to consider electrons belonging to a molecule as particles in a box, where the size of the box is connected to the size of the molecule.
 - This quantum mechanical treatment (see Chpt 12) gives the following formula:

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}$$

- Thus the spacing of two successive energy levels becomes:

$$\begin{aligned} \Delta E &= E_{n+1} - E_n = [(n+1)^2 - n^2] \frac{\hbar^2 \pi^2}{2mL^2} \\ &= (2n+1) \frac{\hbar^2 \pi^2}{2mL^2} \end{aligned}$$

- Since we are dealing with electrons $m = m_e$
- The molecule can be described by a size parameter R such that:

$$\Delta E_{el} \sim \frac{\hbar^2}{m_e R^2}$$

Sample calculation: when $m_e = 9.1 \times 10^{-31}$ kg, $R = 5 \text{ \AA}$, then $\Delta E = 5 \times 10^{-20}$ J or 30 kJ mol⁻¹.

Spacing of Vibrational Energy Levels

- Consider a diatomic molecule as a harmonic oscillator.

- For a harmonic oscillator

$$F = -k(x - x_0)$$

$$E = T + V = \frac{1}{2}\mu \left(\frac{dx}{dt} \right)^2 + \frac{1}{2}k(x - x_0)^2$$

- Since doubling a bond length from R to $2R$ usually results in dissociation of a molecule and the energy required for dissociation is approximately the same order of magnitude as that required for electronic excitation, it may be argued that $\Delta E_{el} \sim k(\Delta R)^2$, therefore:

$$k \sim \frac{\Delta E_{el}}{R^2} \sim \frac{\hbar^2}{m_e R^4}$$

- The energy for the n^{th} level of a harmonic oscillator are given by:

$$E_n = (n + \frac{1}{2})\hbar\omega$$

where:

$$\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{\hbar^2}{m_e R^4 \mu}}$$

- Thus:

$$\Delta E_{vib} = \hbar \left(\frac{k}{\mu} \right)^{1/2} = \frac{\hbar^2}{R^2} \left(\frac{1}{m_e \mu} \right)^{1/2}$$

- If the molecule under consideration is a homonuclear diatomic with each atom of mass M then:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{MM}{M + M} = M/2$$

- Then:

$$\Delta E_{vib} = \frac{\hbar^2}{R^2} \left(\frac{2}{m_e M} \right)^{1/2} = \left(\frac{2m_e}{M} \right)^{1/2} \Delta E_{el}$$

Spacing of Rotational Energy Levels

- Assume the diatomic molecule is a rigid rotor.

- The quantum mechanical treatment of a rigid rotor gives:

$$E_J = \frac{J(J+1)\hbar^2}{2\mu R^2}$$

as the energy of the J^{th} energy level.

- Therefore the spacing between adjacent levels are:

$$\Delta E_{rot} = [(J+1)(J+2) - J(J+1)] \frac{\hbar^2}{2\mu R^2}$$

$$\Delta E_{rot} = 2(J+1) \frac{\hbar^2}{2\mu R^2}$$

$$\Delta E_{rot} \sim \left(\frac{m_e}{M}\right) \Delta E_{el}$$

$$\Delta E_{el} : \Delta E_{vib} : \Delta E_{rot} :: 1 : \left(\frac{m_e}{M}\right)^{1/2} : \left(\frac{m_e}{M}\right)$$

Small Molecule Energy Levels - Diatomics

- Must consider first the electronic configuration for the molecular orbitals.
 - This can be described with molecular quantum numbers analogous to atomic quantum numbers

Molecular	Atomic
Σ	S
Λ	L
Ω	J

- This time Σ does not represent total spin, but rather that component of spin along the bond axis of the molecule. S is still used for total spin.
- The same information can be represented in a “Term Symbol”:

$$^{2S+1}\Lambda_{\Sigma+\Lambda}$$

Internal Energy of a Molecule

- Consider diatomic molecule AB in the ground electronic state with a known intramolecular potential $V(R)$ where R is the separation of atom A from atom B.
- Recall the Born-Oppenheimer (B-O) approximation which allows the separation of nuclear and electronic degrees of freedom because nuclei are over three orders of magnitude heavier than electrons.
- The total nuclear energy may be expressed in terms of the Hamiltonian:

$$\hat{H}_{nuc} = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 + V(R)$$

- The first term is the kinetic energy operator for atom A,
 - The second term is the kinetic energy operator for atom B,
 - The third term is the potential energy operator.
- ∇ is pronounced “nabla” and, for a particle in (x,y,z) space, ∇^2 is:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- ∇^2 is also known as “del squared” or the Laplacian operator.
- Now the Hamiltonian needs to be transformed to center-of-mass coordinates for the diatomic AB. This yields:

$$\hat{H}_{nuc} = -\frac{\hbar^2}{2\mu}\nabla_R^2 + V(R)$$

where

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

or

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

and

$$\nabla_R^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right]$$

- The quantum mechanical solution of this equation has the form:

$$\Psi_N(R, \theta, \phi) = \psi(R) Y_{J,M}(\theta, \phi)$$

where:

- $Y_{J,M}(\theta, \phi)$ is the spherical harmonic function and describes the nuclear rotation associated with total angular momentum quantum number J and its projection quantum number M .
- $\psi(R)$ describes the nuclear vibrational motion.
- When the wavefunction can be factored, the radial and angular components can be solved separately.
 - Thus the radial Schrödinger equation (RSE) can be written for a diatomic molecule:

$$E\psi = -\frac{\hbar^2}{2\mu R^2} \left[\frac{d}{dR} \left(R^2 \frac{d\psi}{dR} \right) \right] + \left[\frac{J(J+1)\hbar^2}{2\mu R^2} + V(R) \right] \psi$$

- This equation is of the same form as the radial equation for the H atom (which can be solved exactly):

$$E\Psi = -\frac{\hbar^2}{2\mu r^2} \left[\frac{d}{dr} \left(r^2 \frac{d\Psi}{dr} \right) \right] + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] \Psi$$

where

$$V(r) = \frac{e^2}{4\pi\epsilon_0 r}$$

- For the diatomic radial equation, the equation can be transformed into a simple form by considering the function $\chi(R) = R\psi(R)$. Thus the equation becomes:

$$E\chi(R) = -\frac{\hbar^2}{2\mu} \frac{d^2\chi(R)}{dR^2} + \left[\frac{J(J+1)\hbar^2}{2\mu R^2} + V(R) \right] \chi(R)$$

- The term inside the brackets can be considered as an effective potential. Each value of J gives a different equation and a different family of mathematical solutions (vibrational energy levels).

Expanding the Potential

- The potential may be expanded into a power series.

- The variable is:

$$\rho = R - R_e$$

where R_e is the equilibrium separation and ρ/R_e is small.

- Then

$$V(R) = V(R_e) + V'(R_e)\rho + \frac{1}{2}V''(R_e)\rho^2 + \dots$$

and

- $V(R_e) \equiv V_e = \text{a constant}$
- $V'(R_e) \equiv (dV/dR)_{R=R_e} = 0$ since R_e is the position of the minimum
- $V''(R_e) \equiv (d^2V/dR^2)_{R=R_e} = k$ where k is the harmonic force constant.
- If ρ is small and the higher order derivatives are small, then:

$$V(R) = V(R_e) + \frac{1}{2}k\rho^2$$

This can be recognized as the equation of a parabola and is the **harmonic oscillator** potential. **This is approximation 1.**

- Since $dR = d\rho$ the RSE can be written in terms of ρ :

$$E\chi(\rho) = -\frac{\hbar^2}{2\mu} \frac{d^2\chi(\rho)}{d\rho^2} + \left[\frac{J(J+1)\hbar^2}{2\mu(\rho + R_e)^2} + V_e + \frac{1}{2}k\rho^2 \right] \chi(\rho)$$

- Now consider:

$$\begin{aligned} \frac{1}{(\rho + R_e)^2} &= \frac{1}{R_e^2} \left[\frac{1}{(1 + \rho/R_e)^2} \right] \\ &\cong \frac{1}{R_e^2} \left[1 - 2\left(\frac{\rho}{R_e}\right) + 3\left(\frac{\rho}{R_e}\right)^2 - \dots \right] \end{aligned}$$

- If $\rho \ll R_e$, then a **second approximation (rigid rotor)** can be made to keep only the first term. Thus the RSE becomes:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\chi}{d\rho^2} + \left\{ \left[\frac{J(J+1)\hbar^2}{2\mu R_e^2} + V_e - E \right] + \frac{1}{2}k\rho^2 \right\} \chi = 0$$

- The vibrational energy E_{vib} is defined as:

$$E_{vib} = E - V_e - \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

where

- E = the **total molecular energy** (not including translational energy).
- V_e = the **total electronic energy plus nuclear repulsion potential energy** at R_e
- $\frac{J(J+1)\hbar^2}{2\mu R_e^2}$ = the **rotational energy of a rigid rotor diatomic** with quantum number J .
- Thus the RSE becomes:

$$-\frac{\hbar^2}{2\mu} \frac{d^2\chi}{d\rho^2} + \frac{1}{2}k\rho^2\chi = E_{vib}\chi$$

which is the Schrödinger equation for the harmonic oscillator.

This is the rigid rotor harmonic oscillator approximation

The energy expressions become:

$$E_{rot}(J) = \frac{J(J+1)\hbar^2}{2\mu R_e^2}, \quad J = 0, 1, 2, 3, \dots$$

$$E_{vib}(v) = \hbar \left(\frac{k}{\mu} \right)^{1/2} \left(v + \frac{1}{2} \right), \quad v = 0, 1, 2, 3, \dots$$

$$E_{el}(n) = V_e \text{ for state } n$$

such that

$$E = E_{el} + E_{vib} + E_{rot}$$

Spectra are full of evidence that molecules are not rigid rotor, harmonic oscillators. Therefore need corrections:

- Recall

$$V(R) = V(R_e) + V'(R_e)\rho + \frac{1}{2}V''(R_e)\rho^2 + \dots$$

- The deviations from the harmonic potential can be treated as **anharmonic corrections**.
- Vibrational energy level spacing becomes smaller as the vibrational quantum number increases, therefore the anharmonic corrections are negative and are expressed as expansion of $(v + \frac{1}{2})$
- Corrections to rotational energy need to include *centrifugal distortion* and *vibration-rotation coupling*.
 - Correction for centrifugal distortion are expressed as a power series in $J(J+1)$.
 - Correction for vibration-rotation coupling is expressed as a power series in terms of $(v + \frac{1}{2}) J(J+1)$.
- Spectroscopists usually express energy as wave-numbers in units of cm^{-1}
 - Recall that:

$$\bar{\nu} = \frac{1}{\lambda} = \frac{E}{hc}$$

- Since $h = 6.626 \times 10^{-34} \text{ Js}$ and $c = 2.998 \times 10^{10} \text{ cm s}^{-1}$, the conversion factor is $1.986 \times 10^{-23} \text{ J/cm}^{-1}$.
- Therefore, from this point on, spectroscopic parameters will be considered in units based on cm^{-1}

The Dunham Expansion

- Consider the Dunham Expansion, a general expression of the energy of a diatomic molecule.

$$\begin{aligned} E(v, J) = & Y_{00} + Y_{10} \left(v + \frac{1}{2} \right) + Y_{01} J(J+1) \\ & + Y_{20} \left(v + \frac{1}{2} \right)^2 + Y_{02} [J(J+1)]^2 \\ & + Y_{11} \left(v + \frac{1}{2} \right) [J(J+1)] + Y_{30} \left(v + \frac{1}{2} \right)^3 + \dots \end{aligned}$$

- The quantum numbers are dimensionless
- The Y 's are in units of cm^{-1}
- This notation is more recent (1932) than the “traditional” spectroscopic notation. It is also more systematic.

Traditional Spectroscopic Notation

- Total energy is written as:

$$E_{vib,rot} = G(v) + F_v(J)$$

where:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \dots$$

and:

$$F_v(J) = B_v J(J+1) - D_v [J(J+1)]^2$$

with:

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \dots$$

and:

$$D_v = D_e + \beta_e \left(v + \frac{1}{2} \right) + \dots$$

Spectrum of Na_2 (*Making sense of table 19.3*)

- Information of note:
 - Reduced mass
 - Dissociation energy D_0 with respect to the zero point energy of the ground state electronic curve.
 - Ionization potential
- Also note that there is missing information.
- Electronic states are listed in descending order, with the ground state at the bottom.
 - T_e is the electronic energy, with reference to the bottom of the potential curves (i.e. $V_e = V(R_e)$).
 - Each row of the table corresponds to a particular electronic state.
 - Spectroscopic constants (cm^{-1}) given in traditional notation, with additional terms (if any) in the footnotes.
 - Then dissociation energy, D_e , with respect to the bottom of the well.
 - And R_e , the equilibrium separation.
 - Followed by notes on allowed transitions and references.

Calculation of Transition Frequencies

- Use the information in the table to calculate the energy associated with the (electronic, vibrational, rotational) state of interest.
- More conventions:
 - '' (double prime) refers to the state of lower electronic energy.
 - ' (single prime) refers to the state of higher electronic energy.

- Consider the transition from $(v'' = 0, J'' = 0)$ of the ground electronic state to $(v' = 0, J' = 0)$ of the first excited electronic state:

$$\begin{aligned}\nu_{00} &= E' - E'' \\ &= T'_e + G'(v' = 0) - [T''_e + G''(v'' = 0)] \\ &= (T'_e - T''_e) + \frac{\omega'_e - \omega''_e}{2} - \frac{\omega'_e x'_e - \omega''_e x''_e}{4}\end{aligned}$$

- For higher v or J levels, must consider anharmonicity.

Diatomic Rotational Spectroscopy

- Spectra are simplified considerably by selection rules.
 - Selection rules arise from the dipole transition moment
- For a heteronuclear diatomic, there is a permanent dipole therefore in the ground electronic state, the rotational selection rule is:
 - $\Delta J = J' - J'' = \pm 1$
- For a homonuclear diatomic, there is no permanent dipole, therefore there is no true rotational spectrum (to first order).

Predicting a Pure Rotational Absorption Spectrum

- Selection rule is $\Delta J = \pm 1$
- Initial state is the lower state (v'', J'')

$$E(v'', J'') = T''_e + G(v'') + F_{v''}(J'')$$

- The final state is the upper state (v', J')

$$E(v', J') = T'_e + G(v') + F_{v'}(J')$$

- Since the electronic state and the vibrational state do not change, the observed frequency is:

$$\Delta E = E(J') - E(J'') = F_v(J') - F_v(J'')$$

Example of Calculated Rotational Spectrum

- Assume $v = 0$
 - This is reasonable if the sample is at thermal equilibrium.
- Therefore

$$F_v = B_v J(J+1) - D_v [J(J+1)]^2$$

$$B_v = B_e - \frac{\alpha}{2}$$

$$D_v = D_e + \frac{\beta}{2}$$

- Consider the transition $J = 0 \rightarrow J = 1$

$$\Delta E = 2(B_e - \frac{\alpha}{2}) - 4(D_e + \frac{\beta}{2})$$

- The next line in the spectrum will be $J = 1 \rightarrow J = 2$

$$\Delta E = 4(B_e - \frac{\alpha}{2}) - 32(D_e + \frac{\beta}{2})$$

- And the next line $J = 2 \rightarrow J = 3$

$$\Delta E = 6(B_e - \frac{\alpha}{2}) - 108(D_e + \frac{\beta}{2})$$

- Generally:

$$\Delta E = 2(J'' + 1)(B_e - \frac{\alpha}{2}) - 4(J'' + 1)^3(D_e + \frac{\beta}{2})$$

This gives line positions in the spectrum.

Line Spacings in a Pure Rotational Spectrum

- Consider two adjacent lines for $\Delta v = 0$:

$$\begin{aligned} \Delta(\Delta E) &= 2(J'' + 2)(B_e - \frac{\alpha}{2}) - 4(J'' + 2)^3(D_e + \frac{\beta}{2}) \\ &\quad - [2(J'' + 1)(B_e - \frac{\alpha}{2}) - 4(J'' + 1)^3(D_e + \frac{\beta}{2})] \end{aligned}$$

or

$$\begin{aligned} \Delta(\Delta E) &= 2(B_e - \frac{\alpha}{2}) \\ &\quad - 4[(J'' + 2)^3 - (J'' + 1)^3](D_e + \frac{\beta}{2}) \end{aligned}$$

- Thus the lines in the spectrum are nearly evenly spaced, with the deviation due to the centrifugal distortion.
- Spacing between adjacent lines is approximately $2(B_e - \frac{\alpha}{2})$

To interpret a spectrum, do this “backwards”

- Measure spacing between lines for a particular Δv .
- Fit to equation of appropriate curve to get spectroscopic coefficients.

Interpretation of Vibrational-Rotational Spectra

- Heteronuclear diatomic
- Infrared spectra, therefore a vibrational transition has occurred.
 - Selection rules for strongly allowed transitions are: $\Delta v = \pm 1$; $\Delta J = \pm 1$
 - Weakly allowed transitions are:

$$\Delta v = \pm 2, \pm 3, \dots$$

but with diminished intensity.

- Absorption spectra, therefore final state has a higher energy than the initial state
 - Transitions observed are $\Delta v = 1$; $\Delta J = \pm 1$
 - Initial state is $v = 0$
- Recall energy of a $(0, J'')$ state (neglecting higher order corrections):

$$E(0, J'') = G(0) + F_0(J'')$$

$$= \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + (B_e - \frac{\alpha_e}{2})J''(J'' + 1)$$

- And energy of a $(1, J')$ state is:

$$\begin{aligned} E(1, J') &= G(1) + F_1(J') \\ &= \frac{3}{2}\omega_e - \frac{9}{4}\omega_e x_e + (B_e - \frac{3\alpha_e}{2})J'(J' + 1) \end{aligned}$$

- Therefore the energy of a line is:

$$\begin{aligned} E(1, J') - E(0, J'') &= \omega_e - 2\omega_e x_e \\ &\quad + B_e[J'(J' + 1) - J''(J'' + 1)] \\ &\quad - \frac{3\alpha_e}{2}J'(J' + 1) + \frac{\alpha_e}{2}J''(J'' + 1) \end{aligned}$$

- If $\Delta J = 1$ (R branch):

$$\begin{aligned} E(1, J'' + 1) - E(0, J'') &= \omega_e - 2\omega_e x_e \\ &\quad + 2B_e(J'' + 1) - \alpha_e((J''^2 + 4J'' + 3)) \\ &= \omega_e - 2\omega_e x_e + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e J''^2 \end{aligned}$$

- Defining $m = J'' + 1$ and $\nu_0 = \omega_e - 2\omega_e x_e$, this becomes:

$$\Delta E = \nu_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2$$

- If $\Delta J = -1$ (P branch):

$$\begin{aligned} E(1, J'' - 1) - E(0, J'') &= \omega_e - 2\omega_e x_e \\ &\quad - 2B_e J'' - \alpha_e((J''^2 - 2J'')) \\ &= \omega_e - 2\omega_e x_e + (2B_e - 2\alpha_e)J'' - \alpha_e J''^2 \end{aligned}$$

- Defining $m = J''$ and $\nu_0 = \omega_e - 2\omega_e x_e$, this becomes:

$$\Delta E = \nu_0 + (2B_e - 2\alpha_e)m - \alpha_e m^2$$

- Since $\Delta J = 0$ is not allowed, the Q branch is missing.

- If the Q branch existed, it would be at

$$E(1, J'') - E(0, J'') = \omega_e - 2\omega_e x_e$$

- Line Spacings:

- R Branch ($\Delta J = 1$)

$$\begin{aligned} \Delta(\Delta E) &= (2B_e - 4\alpha_e) - \alpha_e(2J'' + 1) \\ \Delta(\Delta E) &= (2B_e - 3\alpha_e) - 2\alpha_e m \end{aligned}$$

- P Branch ($\Delta J = -1$)

$$\begin{aligned} \Delta(\Delta E) &= (2B_e - 2\alpha_e) - \alpha_e(2J'' + 1) \\ \Delta(\Delta E) &= (2B_e - 3\alpha_e) - 2\alpha_e m \end{aligned}$$

Therefore, a plot of the spacings of adjacent lines against m will give a slope of $-2\alpha_e$ and an intercept of $(2B_e - 3\alpha_e)$

Interpretation of Electronic-Vibrational Spectra

- Consider two electronic states of a diatomic molecule:

- Initial state is the lower state (v'', J'')

$$E(v'', J'') = T_e'' + G(v'') + F_{v''}(J'')$$

- The final state is the upper state (v', J')

$$E(v', J') = T_e' + G(v') + F_{v'}(J')$$

- The selection rules for electronic transitions do not place restrictions on changes in vibration.
- The limitations of instrumentation means that rotational lines usually are not resolved.
 - Discussion will be restricted to electronic and vibrational changes.
- The likelihood of vibrational changes is governed by Franck-Condon Principle
 - Electrons are three to four orders of magnitude lighter than are nuclei.
 - Electronic transitions occur so fast that the nuclei do not get a chance to move (Born-Oppenheimer approximation).
 - “Vertical” transitions are favoured.

- The wavenumber associated with a transition is:

$$\begin{aligned}\bar{\nu} &= E' - E'' = T_e' - T_e'' + G'(v') - G''(v'') \\ &= \bar{\nu}_{el} + \omega_e'(v' + \frac{1}{2}) - \omega_e''(v'' + \frac{1}{2}) \\ &\quad - \omega_e'x_e'(v' + \frac{1}{2})^2 + \omega_e''x_e''(v'' + \frac{1}{2})^2\end{aligned}$$

- Therefore, just need to assign v' and v'' and fit.
- But, how do you know when the assignment is correct?
- Consider the spacing of lines within each “family”.
 - For a given v'' , the spacing between the lines for $v'' \rightarrow v'$ and $v'' \rightarrow v' + 1$ is:

$$\begin{aligned}\Delta\bar{\nu}(v'') &= \bar{\nu}(v' + 1, v'') - \bar{\nu}(v', v'') \\ &= \omega_e' - 2\omega_e'x_e'(v' + 1)\end{aligned}$$

- For a given v' , the spacing between the lines for $v'' + 1 \rightarrow v'$ and $v'' \rightarrow v'$ is:

$$\begin{aligned}\Delta\bar{\nu}(v') &= \bar{\nu}(v', v'' + 1) - \bar{\nu}(v', v'') \\ &= \omega_e'' - 2\omega_e''x_e''(v'' + 1)\end{aligned}$$

- Therefore can test the line assignments with the Deslandres table.

Construction of the Deslandres Table

- Column label is v'' .
- Row label is v' .

- Using figure in lab handout for reference, Look for patterns in your spectrum to make a provisional assignment.
 - Note direction of horizontal axis.
 - Note that spectrum is in terms of wavelength.
- Using a spreadsheet, have three columns for each v'' and two rows for each v' .
 - In the cells corresponding first of the three columns and the first of the two rows, enter the wavelength of the assigned lines.
 - In the next column to each entry, calculate the corresponding wavenumber.
 - In the third column, calculate the difference between successive v'' line positions in wavenumbers.
 - In the second row, second columns (with respect to each spectral line) calculate the difference between successive v' line positions in wavenumbers.
- Inspect the table for anomalies.

What to do About Anomalies

- Anomalies show up as an irregularities in the “pattern”.
 - Expect $\Delta\bar{\nu}(v')$ (or $\Delta\bar{\nu}(v'')$) to become smaller as v' (or v'') gets larger.
 - Anomalies are due to error in peak assignment
 - May also be due to errors in the peak position
- Errors in peak assignments often show up as “jumps” in the pattern.
- Errors in peak position are due to the limitations of the peak-finding algorithm and show up as “zigzags”.
- Once peak assignments are correct, then spectroscopic parameters may be extracted from the Birge-Sponer plots since:

$$\Delta\bar{\nu}(v') = \omega'_e - 2\omega'_e x'_e (v' + 1)$$

$$\Delta\bar{\nu}(v'') = \omega''_e - 2\omega''_e x''_e (v'' + 1)$$

- From this, information about the interaction potential may be inferred.
 - Since this is general, ' and '' are dropped.

Estimation of Dissociation Energy

- At the dissociation energy, the spacing between successive vibrational levels goes to zero.

$$\Delta\bar{\nu}(v_{max}) = \omega_e - 2\omega_e x_e (v_{max} + 1) = 0$$

- Solving for v_{max} gives:

$$v_{max} = \frac{1}{2x_e} - 1$$

and thus

$$G(v_{max}) = \omega_e \frac{(1/x_e - x_e)}{4} = D_e$$

This is the dissociation energy from the bottom of the well.

- For D_0 , the dissociation energy from the $v = 0$ state, this must be corrected for the zero point energy, giving:

$$D_0 = \omega_e \frac{(1/x_e - 2)}{4}$$

Determination of Morse Potential

- The Morse potential is a model potential form with the characteristics of an anharmonic oscillator.

$$U(r - r_e) = D_e \{ \exp[-\beta(r - r_e)] - 1 \}^2$$

- D_e is the dissociation energy.
- β is determined from D_e and the harmonic oscillator force constant k_e

$$\beta = \left(\frac{k_e}{2hcD_e} \right)^{1/2}$$

- The harmonic oscillator force constant k_e is determined from ω_e :

$$k_e = \mu(2\pi c\omega_e)^2$$

- Potential for both electronic states can be determined.

Potential Energy Surfaces

- If the potential is known, then the spectrum can be calculated.
 - But, can the potential be determined from the spectrum?
- Consider a diatomic molecule in the ground electronic state.
 - Potential known to be repulsive at short range and attractive at long range.
 - Choose a functional form that has the desired properties.
 - Morse potential is one such form.

$$V(R) = D_e \left(1 - e^{-\beta(R-R_e)} \right)^2$$

with only three parameters to be considered.

- How are the spectroscopic coefficients related to the potential?
 - Recall that the harmonic oscillator force constant $k = V''(R_e)$
 - Taking the second derivative of the Morse Potential and evaluating the result at $R = R_e$

$$\left(\frac{d^2V}{dR^2} \right)_{R_e} = 2\beta^2 D_e = k$$

- k can be determined from ω_e :

$$hc\omega_e = \hbar \left(\frac{k}{\mu} \right)^{1/2}$$

- Determination of D_e , depends on how energy levels are considered.
 - Exact QM treatment gives an energy level expression of the form:

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2$$

- Solving for $(v + \frac{1}{2})$ at the dissociation energy and noting that $\omega_e x_e \ll \omega_e$, gives

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

- Now all the information to calculate β is available:

$$\beta = 2\pi c \omega_e \left(\frac{\mu}{2D_e} \right)^{1/2}$$

- The Morse potential does a reasonable job of representing a diatomic potential but it does have drawbacks
 - Because it has only two additional parameters beside R_e , it can represent only the first anharmonic correction.
 - It does not accurately predict spectral lines.
 - It is too “stiff” as a functional form to fit a real potential.

**HERE ENDS
OUR TREATMENT OF SPECTROSCOPY**